

# CHAPTER I

## INTRODUCTION

### 1.1 Introduction.

At present, petroleum industry is one of the essential industry in Thailand as well as in the other countries due to the wide demands for oil and gases as the energy sources for automobiles and machines. In an oil refinery process, there are some toxic gases produced and released as by-products to the atmosphere: hydrogen sulfide ( $H_2S$ ), sulfur dioxide ( $SO_2$ ), carbon monoxide (CO), and hydrocarbon gases.

Carbon monoxide (CO) is colorless, tasteless, and odorless. At high concentrations, it can seriously affect human aerobic metabolism leading to drowsiness, respiratory failure, and death. Carbon monoxide reacts with the hemoglobin of blood to give carboxyhemoglobin, thus reducing the capability of the blood to carry oxygen. Carbon monoxide (CO) can be produced both by natural and by human activities. By natural, the oxidation of methane gas from decaying vegetable and human metabolism is a major source. In the other hand, the carbon monoxide (CO) emission by anthropogenic can be mainly classified into four groups which are transportation sources-primarily gasoline-powered internal combustion engines, fuel combustion in power, industrial processes, and solid-waste disposal and miscellaneous. Carbon monoxide concentrations are especially high in congested urban areas where traffic is heavy and slow-moving. The CO content of the atmosphere would be increasing at the rate of about 0.5 ppm yearly. The air quality standards for CO, in 1970, were established as  $10\text{ mg/m}^3$  (9 ppm) as the maximum eight-hour average and  $40\text{ mg/m}^3$  (35 ppm) as the maximum one-hour average. Numerous detection methods are available for both intermittent (grab) and continuous sampling of CO. These methods use gravimetric, chemical,

electrochemical, and colorimetric processes, including nondispersive infrared (NDIR) which is used for monitoring ambient-air-quality standards (Peavy *et al.* 1985).

Due to increasing amounts of these toxic gases released, a growing concern for environments, and the requirements for better process control, new generations or improved gas sensors are desirable. Some examples are electrochemical sensors, MOS devices with zeolite filters, piezoelectric sensors, and a mixture of sensor types (Bartlett *et al.*, 1989). Normally, gas sensor devices use metallic oxides such as SnO<sub>2</sub> or ZnO as sensing materials. They, however, have many disadvantages; namely, the lack of sensitivity and selectivity at low concentrations, the lack of sensitivity to ambient moisture, and the requirement in many applications to operate at 300°C or above (Garder *et al.*, 1994).

Conductive polymers are potential candidates for sensing materials. There exist two mechanisms to explain how a conductive polymer responds to toxic gases (Maria *et al.*, 1997). If a conductive polymer is exposed to an electron donor gas, for instance, ammonia (NH<sub>3</sub>) or hydrogen sulfide (H<sub>2</sub>S), the electrical conductivity of a p-type conductive polymer will decrease because the number of holes as charge carriers of the doped polymer is reduced resulting from the deprotonation process. If a conductive polymer is exposed to an electron withdrawing gas, in contrast, such as sulfur dioxide (SO<sub>2</sub>) or nitrogen oxide (NO), the electrical conductivity of a p-type conductive polymer will increase because of the augmentation of the number of hole charge carriers of the polymer (Agbor *et al.*, 1995).

## 1.2 Background.

### Conductive Polymer.

Conductive polymer is a novel class of polymers which possesses higher electrical conductivity than ordinary polymers which are usually insulating materials. Electrically conducting polymers can be classified into three groups; ion-polymer solid electrolyte systems, composites of electronically conducting material in non conducting polymers, and polymers that conduct electricity by electronic transport.

The first one, ion-polymer solid electrolyte systems, shows electrical conductivity since polymer molecules can function as solid solvents for salts. One or both of the ions are passed from one polymer molecule, which possesses electron donor coordination sites, to another as the macromolecules undergo a thermally induced motion. Free volume effect is important in ion transport because it provides a pathway through which ions can diffuse. This means that the polymer should have a low glass transition temperature and a low degree of crystallinity.

The second one is the composite of electronically conducting material in a non-conducting polymer made by pyrolysis of graphite or by the incorporation of graphite powder or metal particles into a composite structure. The electronic conductivity depends on contact between the conducting particles. In the preparation process of these materials, a balance between the need for a high conductivity against the deterioration of electrical and other mechanical properties should be concerned. Conducting composite material is widely used in antistatic coating, as packaging materials, as electrodes, and in some devices in the electrical engineering industry (Allcock *et al*, 1991).

Electrically conductive polymer is the last group which displays the extended  $\pi$ -electron conjugation. The incorporation of the conjugation along the backbone is of foremost importance (Mark *et al*, 1986) because it provides

a pathway for electrons to migrate along a polymer chain and to jump from one chain to another chain (Alger, 1989). To convert an insulating polymer, conductivity range  $10^{-10}$  to  $10^5$  S.cm<sup>-1</sup>, to a conductive polymer with near metallic conductivity,  $\sim 1$  to  $10^4$  S.cm<sup>-1</sup>, (Saleaneck, 1991) such as trans- and cis- polyacetylene [(CH)<sub>x</sub>], polypyrrole (Ppy), polythiophene (Pt), poly(p-phenylene)(PPP), poly(p-phenylene vinylene) (PPV), and polyaniline (PANI) (Mark *et al*, 1996), charge transfer agents, dopants, are often required to inject electrons into the delocalized framework or to remove electrons and leave positive holes (Allode *et al*, 1990).

The conductivity,  $\sigma$ , is proportional to the product of the free-carrier concentration,  $n$ , and the carrier mobility,  $\mu$ , as follow Equation:

$$\sigma = ne\mu \quad (1)$$

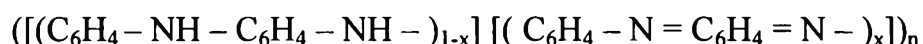
where  $e$  is the unit electronic charge,  $1.6 \times 10^{-9}$ C (Smith, 1974).

The key properties of a conjugated polymer in relation to its potential as a precursor to conducting electrons are *ionization potential*, *electron affinity*, *band width*, and *band gap*. Low value of ionization potential and high electron affinity indicate that a polymer can be easily oxidized (p-doping) and reduced (n-doping), resulting in increases in the carrier concentration,  $n$ , and electrical conductivity. The band width indicates whether the ionized material is conducive to the intrachain charge transport and hence a large band is preferred. Although a conjugated polymer has backbone structure well suited to electron conduction but conductivity is negligibly low since the conjugated polymer may have a relatively large band gap, the energy difference between the energy of the top of the valence band and that of the bottom of the conduction band, so the concentration of free carriers,  $n$ , is very low at normal temperature. In addition, the electron transport properties of conducting polymers are highly dependent upon the structure disorder, doping procedure, and aging (Skotheim *et al*, 1998).

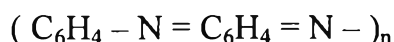
Conductive polymers can be developed commercially as gas sensing materials because of several reasons: light weight, ease of processability, and electronic conductivity. In addition to be used as sensors, they have potential applications in batteries, electronic cells, controlled-release applications, and so on.

### **Polyaniline.**

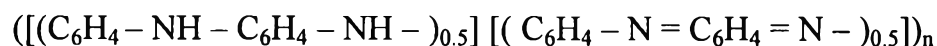
Polyaniline was firstly synthesized by H.Letheby in 1862 to be used as a black ink (Barici *et al*, 1996). It has attracted a considerable attention since MacDiaramid *et al.* reinvestigated this material as a conducting polymer (Cao *et al*, 1989). Polyaniline is a unique and promising candidate for practical applications because it is highly stable in air and soluble in some solvents and it can exhibit dynamic changes in its electronic structure and physical properties with the protonation state (Wan and Li, 1996). It can be synthesized from inexpensive monomer, and the polymerization is straightforward with a high yield. Polyaniline is the simple 1,4 coupling product of monomeric aniline molecules (Lux, 1994). It can be synthesized by either chemically providing a copper powder, or electrochemically giving a cohesive film, or by an oxidative polymerization of aniline in aqueous acid solution (Huang *et al*, 1986). Polyaniline has the generalized composition containing a reduced repeating unit and an oxidized repeating unit. The chemical formula of polyaniline can be described as:



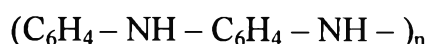
By varying the oxidation level, polyaniline can be converted into 4 different oxidation states. The first one is pernigraniline (x=1):



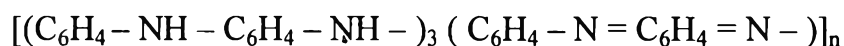
which is of the fully oxidized form having a violet color. The second one is emeraldine base ( $x=0.5$ ):



which is the general state of polyaniline with a dark blue color consisting of alternating oxidized and reduced repeating units. The third one is yellow, a fully reduced form, and is called leucoemeraldine base ( $x=0$ ):

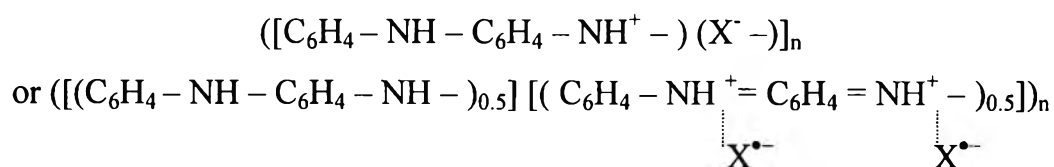


Protoemeraldine base is the last type of polyaniline which has a blue color:



Its color depends strongly on the details of the reaction, for instance, the size of the reaction flask, stirrer speed, and reaction temperature (Lux, 1996).

In general, a polyaniline salt has green color:



Polyaniline salt is obtained through the doping process which converts an emeraldine base into an emeraldine salt. There are two independent doping routes to create an emeraldine salt from an emeraldine base; by an oxidation either electrochemically or chemically, and by protonation through acid-base (Salaneck, 1993). It is normally accepted that protonation of polyaniline leads to the formation of radical cation by an internal redox reaction which causes

the reorganization of electronic structure to give two semiquinone radical cations, called polaronic states (Dhawan *et al*, 1997). The degree of protonation and following electronic conductivity thus become a function of pH (Salaneck, 1993). Oxidation causes a change in the total number of  $\pi$  electrons on the conjugated chains, whilst protonation causes no change in the number of  $\pi$  electrons.

Morphology of polyaniline effectively influences the conductivity of polymer. The more crystalline, the larger conductivity of polymer, that is, the more a metallic-like states displays. The metallic state can be induced by stretching the interchain interaction, increasing the density of crosslinks between fibers, or increasing the localization length. Furthermore, local variations in the extent of hydrogen bonding, the relative proportion of amine to imine linkages, the relative concentration of primary dopants, the inclusions of secondary guest species such as water, and secondary dopants affect the conductivity of polymer as well.

In spite of various benefits of polyaniline, It has some technical difficulties, for example, difficult processability because of its insolubility in most common solvents and other materials (Quillard *et al*, 1994).

### **Conductive Polymer Sensor.**

There are many interesting applications for a conducting polymer, for an example, it can be used as an actuator or a sensor since the conducting polymer can change its properties by incorporation of ions and solvents. Conductive polymer can change its volume depending upon its oxidation state, so it is possible to convert electrical force into mechanical work (Stenger-smith, 1998). Early works reported that some polymers such as polypyrrole, polyaniline, poly-N-methyl pyrrole, and poly-5-carboxyindole could respond to the vapors of alcohol, acetone, and ether. In addition, pyrrole black is sensitive to  $\text{NO}_2$  and  $\text{H}_2\text{S}$  under suitable conditions; these gases react with Ppy

by oxidizing and reducing the Ppy, respectively (Terge *et al*, 1998). Many types of gas sensor are desired to detect gases in various industries and atmosphere: for instance, toxic compounds from bleaching processes in pulp and paper industries, volatile organic compounds from oil and gas industries, and toxic gases from automobiles in urban areas (Howard, 1999).

Polyaniline appears suitable to be used as sensing materials due to its good sensitivity and selectivity (Cao *et al*, 1992). Polyaniline used as sensor material has been shown to be able to detect different vapors like methanol, ethanol, acetone, and benzene (Grummt, 1997), ammonium sensors (Younan, 1995). Polyaniline membranes are far superior in the selectivity for all known gas separation membranes for many simple gas mixtures such as O<sub>2</sub> and N<sub>2</sub> (Kukla, 1996).